Magnetic Structure and Susceptibility of $CoSe_2O_5$: A Low Dimensional Antiferromagnet

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$CoSe_2O_5$ has a crystal structure consisting of zig-zag chains of edge shared CoO_6 octahedra running along the c axis, with the chains separated by $Se_2O_5^{2-}$ units. Magnetic susceptibility measurements indicate a transition at 8.5 K to an ordered state. We investigate here the nature of this magnetic ordering using magnetization and specific heat measurements in addition to powder neutron diffraction. A transition to long-range antiferromagnetic order is found below $T_N = 8.5$ K as identified by magnetic susceptibility measurements and magnetic Bragg reflections, with a propagation vector $\mathbf{k} = 0$. The magnetic structure shows that the moments align perpendicular to the c-axis, but with the spins canting with respect to the a axis by, alternately, $+8^\circ$ and -8°. Interestingly, the low-field magnetic susceptibility does not show the anticipated cusp-like behavior expected for a well-ordered antiferromagnet. When the susceptibility is acquired under field-cooling conditions under a 10 kOe field, the the usual downturn expected for antiferromagnetic ordering is obtained. Heat capacity measurements at low temperatures indicate the presence of gapped behavior with a gap of 6.5 K.

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I. INTRODUCTION

Recently there has been a significant interest in materials with reduced crystallographic dimensionality because of their strong interplay between charge, lattice, and magnetic degrees of freedom.[1,2] From the perspective of magnetism, one-dimensional chains of spins are especially interesting because of the possibility of competing nearest and next-nearest neighbor exchange interactions.[3] Examples of recently studied compounds with magnetic chains include ones showing geometric frustration, magnetoelectric coupling, and possibly quantum tunneling of the magnetization, as exemplified by $Ca_3Co_2O_6$,[4,5,6] $MnWO_4$,[7] and $LiCu_2O_2$.[3,8]

Here we report on $CoSe_2O_5$, an orthorhombic compound with the *Pbcn* space group, consisting of chains of edge sharing CoO_6 octahedra which zig-zag along the the c axis. Each chain is bound together by $Se_2O_5^{2-}$ units *via* shared oxygen at the corners of the octahedra. The diselenite units can be visualized as two trigonal pyramids of SeO_3 which share a corner and contain two lone-pairs of electrons which point in antiparallel directions. This connectivity packs the chains in hexagonal arrays and isolates them magnetically. This compound and its structure was reported by Harrison *et al.*[9] but no reports on the properties have been made. We were particularly interested in this compound because of its low dimensionality, the presence of orbitally degenerate octahedral Co^{2+}, and the presence of possibly symmetry reducing lone pairs.

We have used a combination of magnetic susceptibilty and magnetization measurements, powder neutron diffraction, and specific heat measurements to characterize the nature of the magnetic ground state below 8.5 K and at low magnetic fields. We also suggest the presence of more complex ground states at high fields, a subject for future study. The compound displays a spin gap, with the size of the gap being 6.5 K.

II. EXPERIMENTAL METHODS

$CoSe_2O_5$ was prepared following the reported hydrothermal procedure.[9] SeO_2 (5.0 g, Cerac, 99.99%) was dissolved in 15 cm^3 of water and combined with $CoSO_4{\cdot}xH_2O$ (2.0 g, Sigma-Aldrich, 98%). The mixture was sealed in a 23-mL poly(tetrafluoroethylene)-lined pressure vessel (Parr Instruments) and heated to 200 °C for 48 hours. The resulting product consisted of dark purple single crystals averaging 1.5 mm × 1.5 mm × 0.5 mm.

$ZnSe_2O_5$, a non-magnetic analogue to the title compound, was also prepared to give an estimate of the lattice contribution to the specific heat. SeO_2 (0.7317 g, Cerac, 99.99%) was ground in an agate mortar with ZnO (0.2683 g, Sigma-Aldrich, 98%), sealed in a silica tube, and heated at 350°C for 48 hrs.[10] The resulting product consisted of an off-white polycrystalline powder.

Neutron diffraction data were collected on a sample of

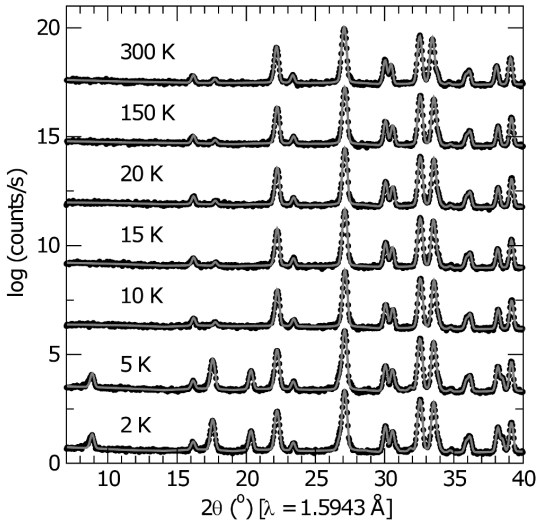

FIG. 1: Low angle region of the powder neutron-diffraction patterns of $CoSe_2O_5$ (D2B, ILL). Note the development of magnetic Bragg peaks in the 5 K and 2 K patterns.

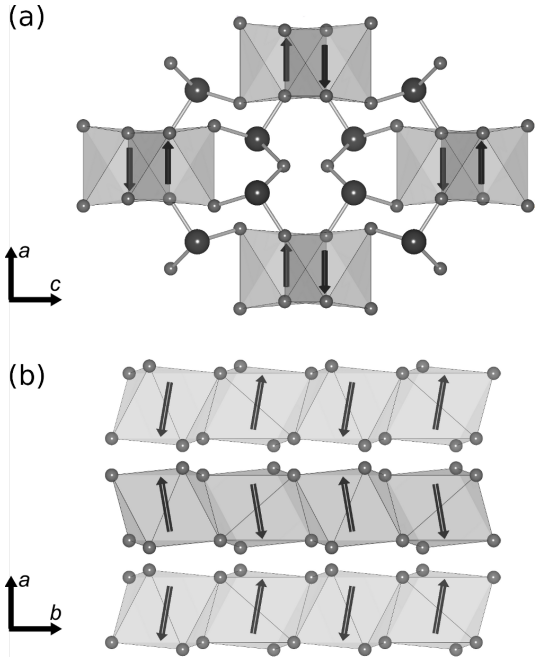

FIG. 2: Magnetic structure of $CoSe_2O_5$ as determined from Rietveld refinements of the neutron diffraction pattern obtained using a $\lambda = 2.4$ Å at 2 K. (a) View down the b-axis of the *Pbcn* structure. (b) View down the c-axis. The small light grey atoms are oxygen while the larger and darker grey atoms are selenium

well-ground single crystals at the D2B powder diffractometer at the Institut Laue-Lagnevin (ILL), France[11] using a wavelength of 1.5943 Å. The wavelength of the incident neutrons was determined by refining the data obtained at 300 K and fixing the cell parameters to the values determined from a room temperature x-ray diffraction pattern collected on a Philips XPERT MPD diffractometer operated at 45 kV and 40 mA. In order to achieve a better fit to the lowest lying magnetic reflections, a diffraction pattern was also collected at 2 K using a wavelength of 2.399 Å.

Temperature dependence of the DC magnetization were measured on well-ground powder samples using a Quantum Design MPMS 5XL SQUID magnetometer. Powders were preferred since the shape and dimensions of the crystal made it dificult to align a single crystal with respect to the field direction. The specific heat data was collected on a 9.5 mg single crystal using the semi-adiabatic technique as implemented in a Quantum Design Physical Property Measurement System (PPMS), under zero applied field, as well as as under a 50 kOe field. The measurement on non-magnetic $ZnSe_2O_5$ was made by mixing the compound with equal parts by mass of Ag powder and pressing into a pellet in order to improve thermal coupling. The contribution from Ag was measured separately and subtracted.

III. RESULTS AND DISCUSSION

The nuclear and magnetic structure of $CoSe_2O_5$ were refined using the Rietveld method as implemented in the FULLPROF software suite.[12] The peak shape was described using the Thompson-Cox-Hastings pseudo-Voigt function, and the background was fit by interpolation between regions showing no Bragg reflections. The crystal structures were analysed based on the model proposed by Harrison *et al.*[9], although it should be noted that we use the standard setting of space group number 60 (*Pbcn*) instead of the alternate *Pnab* description originally used. A summary of key refinement results is shown in table I and in table II. For the magnetic structure, a group theoretical analysis was performed using representational analysis as implemented in the program SARAh[13] was used to determine all of the possible spin configurations which were compatible with the crystal symmetry.

The thermal evolution of the neutron-diffraction patterns collected from 300 K to 2 K are shown in fig. 1. Three magnetic reflections appear below 10 K at 8°, 17°, and 20°. These three peaks could only be fit simultaneously by using the basis vectors of the irreducible representation Γ_8. The resulting magnetic structure associated with Γ_8 and refined from the 2.4 Å data is illustrated in fig. 2. Each chain of Co moments align antiferromagnetically down the length of the chain and with respect to the neighboring chains. The moments cant in the ac plane, forming, alternately, angles of $+8°$ and $-8°$ with respect to the a axis. The moments have no component along b. The magnetic moment on every Co atoms refined to a value of $3\,\mu_B$ at 2 K using the $\lambda = 2.399$ Å neutron diffraction data. This corresponds to three unpaired spins per Co atom in the ordered antiferromagnetic structure.

The high temperature region (350 K to 400 K) of the

TABLE I: Summary of results from the Rietveld structure refinement of the variable temperature neutron diffraction patterns

	300 K	150 K	20 K	15 K	10 K	5 K	2 K	2.4 (Å)
a (Å)	6.7911	6.7890 (1)	6.7900 (2)	6.7897 (2)	6.7892 (2)	6.7897 (2)	6.7893 (2)	6.78877 (2)
b (Å)	10.366	10.353 (2)	10.3524 (2)	10.3522 (2)	10.3516 (2)	10.3529 (1)	10.3523 (1)	10.35166 (4)
c (Å)	6.0750	6.0580 (2)	6.0515 (1)	6.0514 (1)	6.0512 (1)	6.0527 (2)	6.0524 (1)	6.05195 (2)
M (μ_B)						2.80	2.84	3.04
V (Å^3)	427.66	425.80(2)	425.38(2)	425.34(2)	425.28(2)	425.47(2)	425.39(2)	425.31(3)
R_{Bragg} (%)	2.94	2.38	2.35	2.39	2.43	2.34	2.43	2.39
R_{magn} (%)						5.06	5.31	4.76
χ^2	2.87	2.78	2.92	2.81	2.90	3.11	3.11	1.60

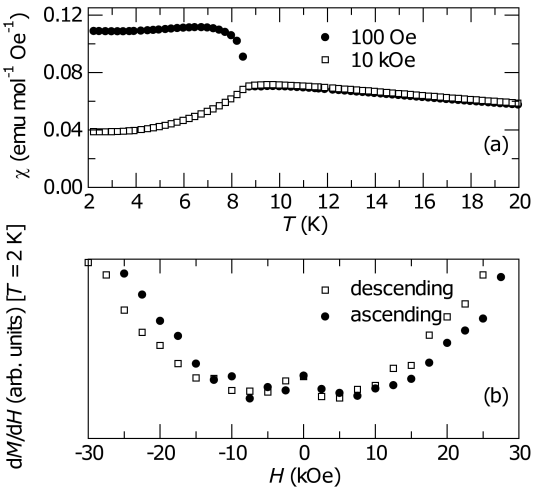

FIG. 3: (a) Magnetic susceptibility a powder sample of $CoSe_2O_5$ acquired after field cooling under fields of 100 Oe and 10 kOe. Note the existence of a weak ferromagnetic component in the low-field data, which does not appear under the higher magnetic fields. Plot of dM/dH at $T = 2$ K showing the existence of a field-induced magnetic transition for fields near $H = 5$ kOe.

inverse susceptibility was fit to the Curie-Weiss equation, $C/(T-\Theta_{CW})$, to obtain the effective moment μ_{eff} from the Curie constant, and the Curie-Weiss intercept Θ_{CW}. A Curie-Weiss temperature of -34 K and an effective moment of 5.19 μ_B were extracted from the fits to the data collected under a 100 Oe field. This value for the effective is in close agreement for the completely unquenched and decoupled orbital contribution ($L+S$) of 5.2 μ_B expected from octahedrally coordinated Co^{2+} (d^3,$t_{2g}^5e_g^2$). This effective moment also agrees well with the three unpaired electrons refined in the neutron data, confirming that the system is in a high spin state. The frustration index, $f = |\Theta_{CW}|/T_N$, is close to 4 which indicates a moderate degree of frustration in this structure.

Fig. 3(a) shows the temperature dependence of the magnetic susceptibility in small and large external magnetic fields for a powder sample of $CoSe_2O_5$. When cooled in small fields, a sharp jump in the susceptibility is observed below 8.5 K. This behavior is unusual and is not in keeping with the magnetic structure which suggests complete antiferromagnetic ordering of spins. It is proposed that the unusual transition in the susceptibility might be associated with the anisotropic, one-dimensional nature of the magnetic structure, and also perhaps, with the magnetism being centered on ooctahedral Co^{2+} which is orbitally degenerate. Data acquired after field cooling in the larger field of 10 kOe results in the more usual downturn in the susceptibility expected from an exact cancellation of all moments.

To more carefully probe the dependence of the magnetization on magnetic field in the ordered phase, we measured $M(H)$ curves at $T = 2$ K. The low field behaviour can be seen most clearly by plotting the differential magnetization (dM/dH), as shown in fig.3(b), showing a small maximum near $H = 0$, with broad minima near $H = 5$ kOe, with no significant dependence on the direction of the magnetic field sweep. Recall that the canted spin structure observed in the neutron scattering experiment was not subject to any external field. These magnetization measurements suggest that even a small external magnetic field can perturb the spin structure towards a more collinear arrangement. Further neutron scattering studies under a magnetic field are planned to explore the nature of magnetic ordering as a function of both field and temperature.

The temperature dependence of the specific heat C_p of $CoSe_2O_5$ shown in Fig.4 exhibits a lamda-type anomaly around 8.5 K corresponding to the transition to long-range magnetic order observed in the susceptibility and in the neutron diffraction data. Measurements on non-magnetic $ZnSe_2O_5$ give an estimate of the lattice contribution using a three term expansion with the best fit yielding a Debye temperature, Θ_D, of 222 K. An estimate of the change in entropy associated with the magnetic transition can be obtained by integrating $C_{p,mag}/T$ defined between the specific heat data of $CoSe_2O_5$ and $ZnSe_2O_5$. The change in entropy due to the magnetic transition, thus determined, was 5.31 J mol^{-1} K^{-1} which is much smaller than the theoretical value of 11.53 J mol^{-1} K^{-1} predicted by the Boltzmann equation ($\Delta S = R\ln(2S+1)$, $S = 3/2$). The difference between expected and measured magnetic entropy changes could arise from the canted nature of the antiferromag-

TABLE II: Atomic positions and anisotropic thermal parameters of $CoSe_2O_5$ at 300 and 2 K

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				300 K					
Co	0	0.940	0.75	0.0024	0.0001	0.0020		-0.0020	
Se	0.631	0.154	0.968	0.0013	0.0007	0.0051	0.0003	-0.0007	0.0002
O1	0.805	0.210	0.342	0.0027	0.0012	0.0098	0.0003	0.0004	-0.0001
O2	0.5	0.932	0.250	0.0063	0.0010	0.0109		-0.0054	
O3	0.840	0.933	0.452	0.0007	0.0020	0.0067	-0.0015	-0.0017	0.0004
				2 K					
Co	0	0.937	0.75	0.0127	0.0042	0.0128		-0.0014	
Se	0.630	0.154	0.969	0.0099	0.0043	0.0148	0.0002	0.0002	0.0000
O1	0.807	0.211	0.342	0.0109	0.0047	0.0168	0.0000	0.0004	-0.0004
O2	0.5	0.931	0.250	0.0112	0.0043	0.0167		-0.0003	
O3	0.840	0.933	0.451	0.0099	0.0050	0.0167	-0.0004	0.0000	0.0000

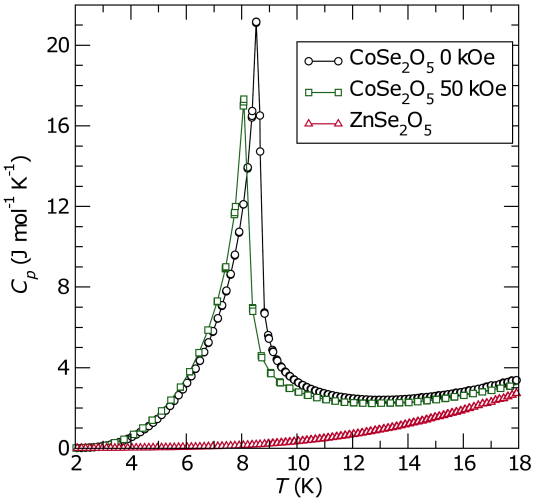

FIG. 4: Temperature dependence of the specific heat of $CoSe_2O_4$ measured on a 9.5 mg single crystal under zero field, and under a $H = 50$ kOe field. A nonmagnetic analogue, $ZnSe_2O_5$, was also measured in order to obtain the lattice contribution to the specific heat. Note the large width of the ordering peak and the release of entropy well above the transition temperature of 8.5 K.

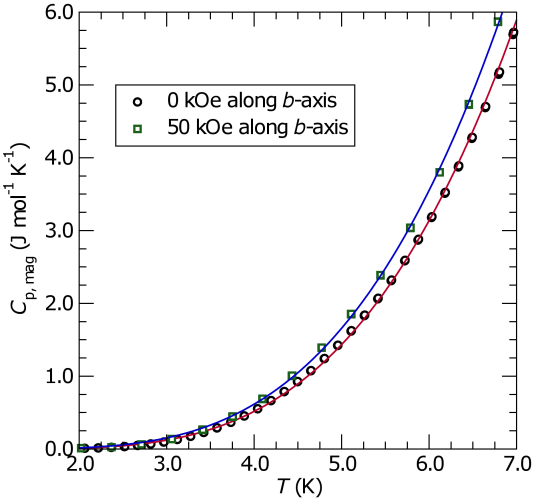

FIG. 5: Magnetic specific heat of $CoSe_2O_4$ below the ordering temperature fitted to the formula for a gapped spin system, $C_p \propto T^3 \exp(-\Delta/k_B T)$, with $\Delta = 6.5$ K for data acquired under $H = 0$ kOe as well as $H = 50$ kOe.

netic ground state. Such diminished entropy changes at magnetic transitions are a common feature of frustrated magnetic materials.

Additionally the large width of the ordering peak at 8 K with a width close to 15 K as compared to simple non-frustrated antiferromagnets, which typically are only a few K wide[14]) also reflects the release of entropy at temperatures higher than the ordering temperature, which is a common feature of geometrically frustrated systems. A slight downward shift of the heat capacity peak was found when a 50 kOe field was applied, but there was little change in the magnitude or shape of the peak.

A fit to the specific heat below the transition temperature could not be obtained using only the T^3 term as would be expected for an antiferromagnet. Instead, the best fit to the data was found when an exponential term was included, using $C_{p,mag} \propto T^3 \exp(-\Delta/k_B T)$.[15] Such an analysis reflects the presence of low-lying magnetic excitations with an energy gap $\Delta = 6.5K$. The presence of spin gaps in one-dimensional magnetic materials is well known.[16]

A. Conclusions

We have examined the magnetic properties of $CoSe_2O_5$ using neutron diffraction, magnetization and magnetic susceptibility, and specific heat measurements. We show that below the magnetic ordering temperature, the one dimensional magnetic chains arrange their moments antiferromagnetically down the length of the chain and with

respect to neighboring chains. The magnetic order in small fields is found to exhibit some canting, although the net moment is zero. Under large applied field, the magnetic behavior changes, pointing to a rich $H - T$ phase diagram in this system. We see evidence for low lying magnetic excitations with a spin gap of 6.5 K, that are also possibly implicated in the field-induced phase transition seen in $\mathrm{d}M/\mathrm{d}H$ *vs.* H at 2 K.

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[1] S.-W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13 (2007).
[2] T. Kimura, Annu. Rev. Mater. Res. **37**, 387 (2007).
[3] S. Park, Y. J. Choi, C. L. Zhang, and S.-W. Cheong, Phys. Rev. Lett. **98**, 057601 (2007).
[4] V. Hardy, S. Lambert, M. R. Lees, and D. McK. Paul, Phys. Rev. B **68**, 014424 (2003).
[5] A. Maignan, V. Hardy, S. Hébert, M. Drillon, M. R. Lees, O. Petrenko, D. M. K. Paul, and D. Khomskii, J. Mater. Chem. **14**, 1231 (2004).
[6] Y. J. Choi, H. T. Yi, S. Lee, Q. Huang, V. Kiryukhin, and S.-W. Cheong, Phys. Rev. Lett. **100**, 047601 (2008).
[7] K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. Lett. **97**, 097203 (2006).
[8] T. Masuda, A. Zheludev, B. Roessli, A. Bush, M. Markina, and A. Vasiliev, Phys. Rev. B **72**, 014405 (2005).
[9] W. T. A. Harrison, A. V. P. McManus, and A. K. Cheetham, Acta Cryst. **C48**, 412 (1992).
[10] G. Meunier and M. Bertaud, Acta Cryst. **B30**, 2840 (1974).
[11] A. W. Hewat and S. Heathman, Acta Cryst. **40**, C364 (1984).
[12] J. Rodríguez-Carvajal, Phys. B. **192**, 55 (1993).
[13] A. S. Wills, Phys. B **276**, 680 (2000).
[14] J. Skalyo and S. A. Friedberg, Phys. Rev. Lett. **13**, 133 (1964).
[15] A. Tari, *The Specific Heat of Matter at Low Temperatures (Hardcover)* (Imperial College Press, 2003).
[16] H. J. Mikeska and M. Steiner, Adv. Phys. **40**, 191 (1991).